III.A.9 Reliability and Durability of Materials and Components for Solid Oxide Fuel Cells

Edgar Lara-Curzio (Primary Contact), Miladin Radovic and Rosa Trejo
Oak Ridge National Laboratory
1 Bethel Valley Rd.
Oak Ridge, TN 37831-6969
Phone: (865) 574-1749; Fax: (865) 574-6098; E-mail: laracurzioe@ornl.gov

DOE Project Manager: Travis Shultz
Phone: (304) 285-1370; E-mail: Travis.Shultz@netl.doe.gov

Objectives

- Characterize mechanical properties-namely elastic moduli, biaxial strength and fracture toughness-of typical anode and electrolyte materials as a function of temperature, level of porosity and environment (reducing or oxidizing).
- Evaluate the magnitude of the residual stress in solid oxide fuel cell (SOFC) anode-electrolyte bilayers.
- Study the effect of thermal cycling on mechanical properties of materials and components for SOFCs.

Approach

- The elastic properties of electrolyte materials (yttria-stabilized zirconia [YSZ] and gadolinium-doped ceria [GDC]) and anode materials (NiO-YSZ and Ni-YSZ) were determined as a function of temperature in different environments using a resonant ultrasound spectrometer (RUS).
- The stochastic distribution of biaxial strengths and fracture toughness of Ni-based anode materials and YSZ electrolytes were determined up to 800°C in H_2 and air. Biaxial strength was determined using the ring-on-ring test method, while fracture toughness was determined according to the double-torsion test method. Experimental fixtures to carry out these tests at elevated temperatures and controlled environments were designed and fabricated at Oak Ridge National Laboratory (ORNL).
- The magnitude of residual stresses in YSZ/NiO-YSZ and YSZ/Ni-YSZ bilayers was determined as a function of temperature by X-ray diffraction (XRD).
- The effect of thermal cycling on the mechanical properties of Ni-based anode materials was investigated by subjecting test specimens to thermal cycling followed by determination of biaxial strength and elastic properties at ambient conditions. Thermal cycling tests were carried out in controlled environments using equipment developed at ORNL.

Accomplishments

- Developed methodologies and experimental facilities for determination of elastic properties, fracture toughness and biaxial strength of SOFC materials in controlled environments as a function of temperature. The methodologies developed are based on the use of RUS, ring-on-ring testing to determine equibiaxial strength and double-torsion to determine fracture toughness.
- Determined the elastic properties, biaxial strength and fracture toughness of tape cast YSZ electrolyte materials, as well as Ni-based anode materials, before and after hydrogen reduction as a function of porosity and temperature, in reducing and oxidizing environments. Strength results were analyzed using Weibull statistics and correlated to microstructural features that act as strength-limiting flaws. Results have been compiled in a user-friendly database.

- Determined changes in the magnitude of the elastic properties of GDC, which are induced by the creation of oxygen vacancies, as a function of exposure time in a reducing environment using RUS.
- Found that microcracking induced by thermal cycling results in a decrease in the elastic properties and strength of Ni-based anode materials.
- Determined the magnitude of residual stresses in YSZ/NiO-YSZ and YSZ/Ni-YSZ bilayers as a function of time in air and in H_2.

Future Directions

- Evaluate the effect of thermal cycling on microstructure, residual stresses and mechanical properties of materials and components for SOFCs.
- Evaluate crack growth rates in YSZ, NiO-YSZ and Ni-YSZ cermets as a function of temperature, porosity and specimen thickness.
- Characterize mechanical properties of cathode material (lanthanum strontium manganite [LSM]) as a function of porosity and temperature.
- Determine the thermal shock resistance of YSZ, Ni-YSZ cermets and YSZ/Ni-YSZ bilayers as a function of temperature, porosity and specimen thickness.
- Evaluate the thermal and creep properties of Ni-YSZ cermets.

Introduction

The durability and reliability of SOFCs depend not only on their electrochemical performance, but also on the ability of their components to withstand mechanical stresses that arise during processing and service. Specifically, the mechanical reliability and durability of SOFCs are determined by the stress distribution in, and the stochastic distribution of strengths of, their components. The stress distribution is a complex function of several parameters, including geometry of the SOFC, temperature distribution and external mechanical loads. Furthermore, residual stresses induced during processing as a result of mismatch in the thermoelastic properties of SOFC components, and evolution of stresses during service, will also affect durability and reliability. The determination of the stress distribution in SOFC materials and components typically requires the use of computational tools (e.g., computational fluid dynamics and finite-element stress analyses), which in turn requires knowing the physical and mechanical properties of the materials and components. The stochastic distribution of strengths of SOFC materials is primarily determined by the type and distribution of strength-limiting flaws, which are either intrinsic to the material or introduced during processing and/or manufacturing. Because flaws can grow with time, it is expected that the distribution of strengths will also evolve with time. Knowledge of the distribution of stresses in, and strengths of, SOFC materials and components is essential to predict their durability and reliability.

Approach

Because most SOFC components consist of thin membranes, the determination of their physical and mechanical properties poses experimental challenges. As part of this project, a resonant ultrasound spectrometer (RUS) was adapted to determine the elastic moduli of SOFC materials at elevated temperatures and in different environments. For example, the elastic moduli of YSZ, GDC, NiO-YSZ and Ni-YSZ were determined in air and in a reducing environment (a gas mixture of 4% H_2 + 96% Ar) at temperatures up to 800°C.

Components of planar SOFCs are mainly subjected to biaxial states of stress that result from the thermal expansion mismatch among the SOFC constituents and from temperature gradients induced during operation. Thus, it has been customary to determine the biaxial strength of SOFC materials using the concentric ring-on-ring flexural-loading configuration. The results of the biaxial test are analyzed using Weibull statistics to determine the parameters of the distribution of strengths, namely Weibull modulus and characteristic strength. In order to evaluate the mechanical properties of Ni-based anode materials in controlled environments (e.g., reducing environment), a unique experimental system was designed and built. The same experimental system is used to determine fracture toughness by the double-torsion test method.

XRD is used to determine the magnitude of residual stresses in bilayers of NiO-YSZ/YSZ as a function of temperature, before and after hydrogen reduction.

Both in stationary and transportation applications, SOFCs will be subjected to thermal cycling associated with start-up and shut-down cycles. The evolution of stresses that will develop in SOFCs as a result of thermal cycling is expected to impact the service life of SOFCs. Thus, experimental equipment for subjecting SOFC components to thermal cycling was developed at ORNL and used to investigate the effect of thermal cycling on the properties of YSZ and NiO-YSZ materials.

Results

The elastic moduli (Young's and shear) of 8 mol% YSZ were found to decrease with temperature between 25 and 600°C. Above 600°C, they were found to increase slightly with temperature up to 1000°C. The peaks associated with resonant frequencies, obtained by RUS, were found to be very broad at temperatures between 200°C and 600°C, suggesting high damping (internal friction) in YSZ at these temperatures. Results of characterization studies using Raman spectroscopy and XRD did not reveal any phase transformation at these temperatures. Thus, the atypical trend of the elastic moduli and the increase in mechanical damping with temperature could be related to mechanically induced mobility of vacancies due to reorientation of elastic dipoles formed between oxygen vacancies and Y (dopant) ions. However, additional work is needed to ascertain the source of this behavior. Similar property-temperature trends were observed for fracture toughness and biaxial strength. The elastic moduli of NiO-YSZ were determined in air as a function of temperature, while the elastic moduli of Ni-YSZ anodes were determined in a gas mixture of 4% H_2 + 96% Ar as a function of temperature. Similar moduli-temperature trends were found for both NiO-YSZ and Ni-YSZ, although the initial decrease in elastic moduli in the temperature interval between 25°C and 600°C is less pronounced than for the case of YSZ.

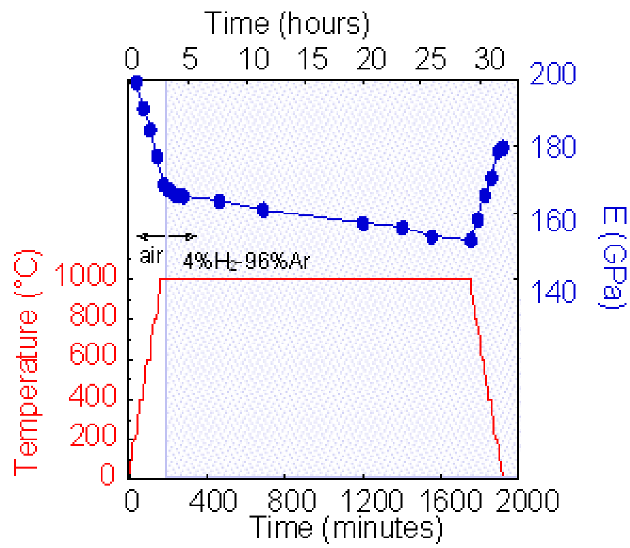

Figure 1. Young's Modulus of GDC as a Function of Temperature and Reduction Time at 1000°C in 4% H_2-96% Ar Gas Mixture

GDC is considered to be a good electrolyte candidate material because of its high ionic conductivity at elevated temperatures. However, when GDC is exposed to low partial pressures of oxygen or reducing environments, the oxygen vacancy concentration in GDC increases with time. For example, it was found (Figure 1) that at a constant temperature of 1000°C in a gas mixture of 4% H_2 + 96% Ar, the Young's modulus of GDC decreases with time as a result of the increase in oxygen vacancy concentration.

The characteristic biaxial strength and Weibull moduli for NiO-YSZ precursor for SOFC anode were determined from the results of ring-on-ring tests in air as a function of porosity for different temperatures. Also, the characteristic biaxial strength and Weibull moduli for Ni-YSZ (Figure 2) were determined in a gas mixture of 4% H_2 + 96% Ar as a function of porosity and temperature. These results show that the characteristic biaxial strength of

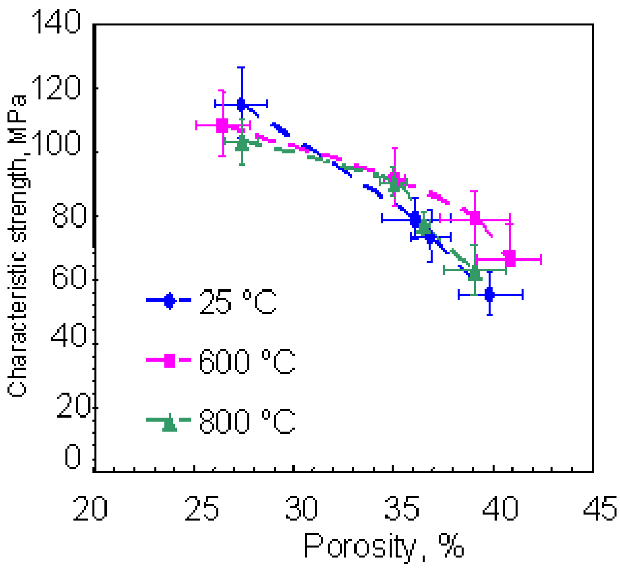

Figure 2. Characteristic Biaxial Strength of Ni-YSZ as a Function of Porosity at 25°C, 600°C and 800°C. Error bars for characteristic strength represent upper and lower 95% confidence bounds. Error bars for porosity represent one standard deviation.

these materials decreases with porosity at all temperatures. On the other hand, the characteristic biaxial strength is slightly higher at elevated temperatures than at room temperature.

Ni-based anode materials were subjected to thermal cycling between 20°C and 800°C in a gas mixture of 4% H_2-96% Ar. Each thermal cycle consisted of heating up to 800°C at a constant rate of 30°C/min, soaking at 800°C for 2 hours and cooling in 90 minutes to ambient temperature at the natural cooling rate of the furnace. The changes induced by thermal cycling on Young's and shear moduli were determined at room temperature by impulse excitation, while biaxial strength was determined by ring-on-ring testing, and the results were analyzed using Weibull statistics. It was found that both the elastic moduli and biaxial strength decrease with the number of thermal cycles, as shown in Figure 3. For example, the characteristic strength of these materials decreased by as much as 25% after 81 cycles. Scanning electron microscopy of the thermally cycled samples revealed the formation of small microcracks, predominantly between YSZ and Ni grains. Thus, the observed changes in mechanical

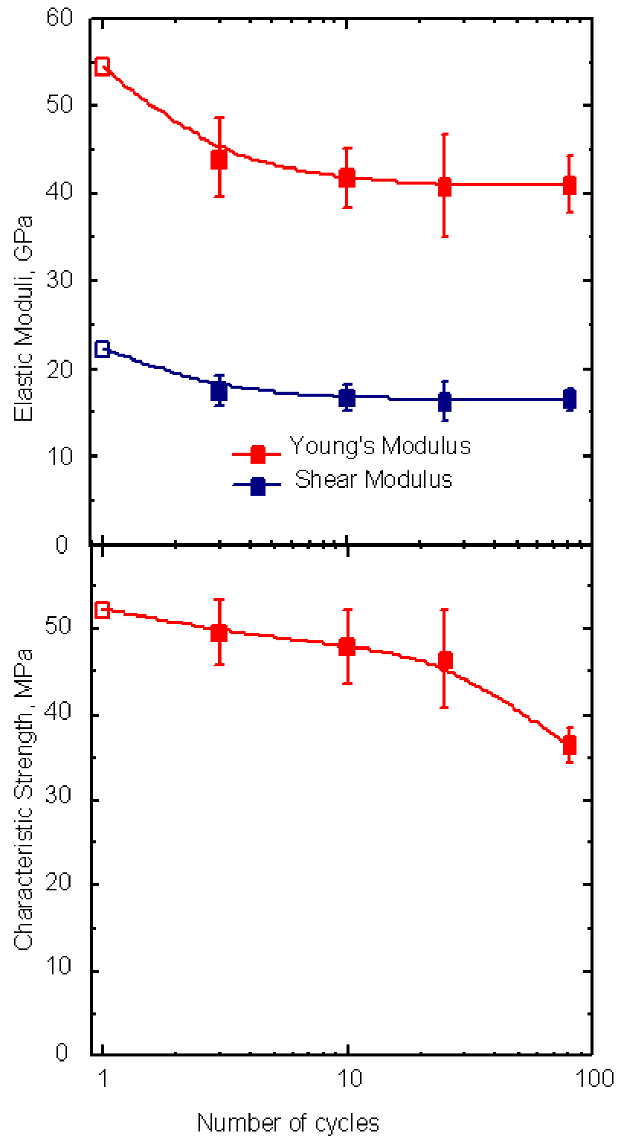

Figure 3. Elastic Properties (top) and Characteristic Biaxial Strength (bottom) of the Ni-YSZ Anode as a Function of Number of Thermal Cycles in Hydrogen

properties can be attributed to the initiation and propagation of microcracks resulting from the difference in thermal expansion behavior of Ni and YSZ grains.

The residual stresses in bilayers of YSZ and NiO-YSZ were determined as a function of temperature from XRD spectra in air and in a gas mixture of 4% H_2 and 96% Ar. The residual stresses in the 10-µm thick layer of YSZ before and after reduction of the NiO-YSZ layer are plotted in

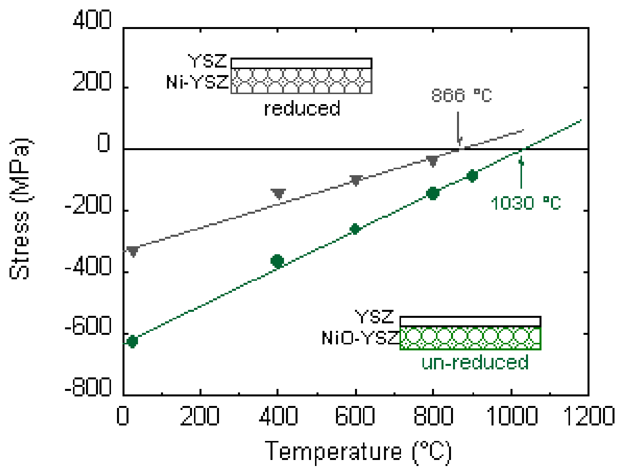

Figure 4. Residual Stresses in Bilayers of YSZ/NiO-YSZ before and after Reduction in Hydrogen

Figure 4. These results show that residual stresses in YSZ are compressive and that in both cases their magnitude decreases with temperature. The compressive residual stresses at room temperature are large, i.e. ≈600 and ≈400 MPa before and after hydrogen reduction, respectively. It was also found that the zero-stress temperature was lower than the co-sintering temperature, most likely due to creep-induced stress relaxation at elevated temperatures.

Conclusions

- It was found that the biaxial strength of both NiO-YSZ and Ni-YSZ decreases with porosity, but does not depend significantly on temperature, at least up to 800°C. The magnitude of the elastic constants and fracture toughness of these materials decreases significantly with temperature in the 25°C-600°C range.
- The elastic properties of YSZ and GDC were characterized as a function of temperature by RUS in air. It was found that Young's and shear moduli of YSZ decrease with temperature between 25°C and 600°C and that they increase slightly with higher temperature up to 1000°C. The Young's modulus of GDC was determined by RUS in air and was found to decrease almost linearly with temperature. When exposed to a gas mixture of 4% H_2-96% Ar at 1000°C, the Young's modulus of GDC was found to decrease continuously with time due to an increase in the concentration of oxygen vacancies.
- The elastic moduli and biaxial strength of Ni-based anode materials were found to decrease with the number of thermal cycles due to formation of small microcracks predominantly between Ni and YSZ grains.
- It was demonstrated that XRD is a powerful technique to determine the magnitude of residual stresses in multilayers of SOFC materials. The residual stresses in NiO-YSZ/YSZ bilayers were determined as a function of temperature before and after hydrogen reduction. It was found that residual stresses in YSZ layer are compressive and relatively large and that their magnitude decreases with temperature. It was also found that magnitude of compressive residual stresses in the YSZ layer decreases after hydrogen reduction.

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